Japanese Patent Laid-Open No. 32274/1978

Laid-Open Date: March 27, 1978

Application No.: 106253/1976

Application Date: September 7, 1976

Request for Examination: Not made

Inventor: Kozo Takahara

Applicant: Idemitsu Kosan Co., Ltd.

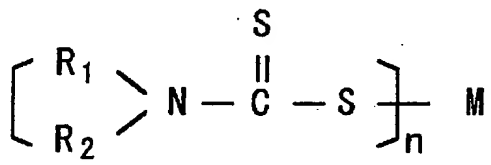
Specification

1. Title of the Invention

Flame Retardant Hydraulic Oil Compositions

2. Claim

1. A flame retardant hydraulic oil composition of a water-glycol type which comprises 0.1wt% or more of a dithiocarbamic acid salt of the general formula:



(wherein R_1 and R_2 represent a C_1-C_{12} hydrocarbon group which may optionally be substituted by a hydroxy group, and R_1 and R_2 may be the same or different; M is a metal of K, Na, Ca, Ba, Zn, Fe, Cu, Ni, Cd, Pb, Bi, Sb, Se, Te, Zr or Mo; n represents a number corresponding to the valence of the metal M).

3. Detailed Description of the Invention

The present invention relates to flame retardant

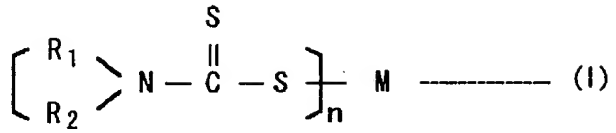
hydraulic oil compositions. More particularly, the invention relates to flame retardant hydraulic oil compositions of a water-glycol type, by using which the fatigue life of the metallic part materials in a hydraulic apparatus can be prolonged.

Today, as the field of industrial applicability of a hydraulic working system has been expanded, the utility of the hydraulic instruments has highly been diversified. The hydraulic oil, accordingly, has been required to have a variety of characteristics responsible to utility. For example, when a metal is rolled under heating in an easily deformed state or melted for molding, it is required that the hydraulic oil used in an equipped machine have the flame-retardant property in view of prevention of the risk of fire preferentially over other characteristics. For the purpose of precautions for safe works and according to the strong guidance of a fire station, there has been much need for the fire retardant hydraulic oil (also called fire-resistant or non-inflammable hydraulic oil) in the market. The commercially available fire retardant hydraulic oils are classified into three types including a phosphate ester type, an emulsion type and a water-glycol type. In general, the phosphate ester type of hydraulic oil has a problem that selection of packing seal materials is restricted. The emulsion type of hydraulic oil has a problem of stability of the emulsification, wherein the

emulsion is readily destroyed. On the other hand, the water-glycol type of hydraulic oil has compatibility with almost of the materials of hydraulic instruments in which a mineral oil type of hydraulic oil is used, and the stability during storage is better. The fatigue life of the water-glycol type hydraulic oil, however, is markedly poorer than the mineral oil hydraulic oil, and as a defect the metal materials are fatigued and destructed at an early stage. P.Kenny and E.D.Yardey (Wear, 20, 110 (1972)) have reported the experimental data relating to the metal fatigue life according to the type of flame retardant hydraulic oils. In accordance of their results, the metal fatigue life in water-glycol type hydraulic oils is about 1/10 of that in the mineral oil type.

In this invention, the above-described defect that the metal fatigue life in water-glycol type hydraulic oils is short was aimed at the subject to be improved, and much effort for research was made towards achieving an improvement. As a result, it was found that employment of a specific additive is capable of removing the defect, and thus the invention was completed. Briefly, the purpose of the invention is to provide water-glycol type hydraulic oil components by using which the metal fatigue life can be prolonged. According to the invention, the purpose of the invention can be achieved by adding 0.1wt% or more of a dithiocarbamic acid salt of the

general formula (I):



to a usual water-glycol type hydraulic oil.

In the general formula (I), R_1 and R_2 represent a C_1-C_{12} hydrocarbon group, and may be the same or different each other, including alkyl, phenyl, alkylated phenyl or benzyl. These hydrocarbon groups may be substituted by an optional number of hydroxy groups for the hydrogen at optional positions. M is a metal of K, Na, Ca, Ba, Zn, Fe, Cu, Ni, Cd, Pb, Bi, Sb, Se, Te, Zr or Mo; n represents an integer corresponding to the valence of the metal M. Such a dithiocarbamic acid salt includes, for example, dialkyl dithiocarbamic acid salt (salt with K, Na, Ca, Ba, Zn, Fe, Cu, Ni, Cd, Pb, Bi, Sb, Se, Te, Zr or Mo), N-ethyl-N-phenyl-dithiocarbamic acid salt (salt with Zn, Fe or Pb), zinc dibenzyldithiocarbamate, or zinc bis(hydroxyethyl)dithiocarbamate, zinc bis-(hydroxypropyl)dithiocarbamate, zinc bis(hydroxy-butyl)dithiocarbamate, zinc bis(hydroxyhexyl)-dithiocarbamate, and the like. The above-described dithiocarbamic acid salt may be added to the water-glycol type hydraulic oil at a rate of 0.1wt% or more, and the effect increases with increase of the amount to be added. However,

since stable solubilization in the basic oil becomes difficult with increase of the added amount, it is preferable to use a solubilizing agent together when the dithiocarbamic acid salt is added at a rate of 1wt% or more depending on its kind. As the solubilizing agent, it is possible to use a conventional emulsifying agent usually used in this technical field, for example, polyoxyethylene alkylamine (P.O.E. stearylamine, P.O.E. oleylamine, P.O.E. laurylamine, etc.; P.O.E. means poloxyethylene), diethylene glycol alkyl ether (D.E.G. monomethyl ether, D.E.G. monoethyl ether, D.E.G. diethyl ether, D.E.G. monobutyl ether, D.E.G. dibutyl ether, ete.; D.E.G. means diethylene glycol), or amino alcohol (1-amino-2-propanol, 2-amino-2-ethyl-1,3-propanediol), and the like. As for these solubilizing agents, it is desired to add a mixture of 1 or more of the agents in a half amount or more (by weight ratio) for the dithiocarbamic acid salt. As for the water-glycol type hydraulic oil used in the invention, those as disclosed in Japanese Patent Laid-Open No. 19280/1976 and USP 2947699 may be used.

The invention will be explained specifically by the following example.

Example

(1) Preparation of Samples

The water-glycol type hydraulic oil of the invention (hereinafter referred to as "Product of Invention") was

prepared by adding a dithiocarbamic acid salt as an essential component to the following oil for comparison if necessary together with a solubilizing agent. Table 1 shows their formulations. As an oil for comparison, a commercially available water-glycol type flame retardant hydraulic oil "Daphne Fire Proof 200G" (trade name)(Idemitsu Kosan) was used.

(2) Method for Evaluation of the Metal Fatigue Life

As an apparatus for measuring the metal fatigue life in order to simulate a course of rolling contact of bearings resulting in the fatigue, an apparatus used in a load-resisting capacity test for oil products (JIS-K-2519) was partially remodeled. This apparatus was remodeled so that the rolling of the balls fitted on the upper shaft rolled the three balls on the lower part. The three balls rotate on their own axis with revolving. The balls furiously vibrate with fatigue to produce noises, accompanied with sudden increase of a helix angel. This time point is regarded as the fatigue life, and the time period required up to this stage is measured for the evaluation. The test was conducted in a condition of a load of 10 kg/cm^2, a revolution number of 770 rpm and an oil temperature of 20°C (at the starting point of the test).

(3) Test Results for the Metal Fatigue Life

Table 1 shows the test results for the metal fatigue life on Product of Invention (Sample nos. 2-20) and the oil for comparison (Sample no. 21). In Sample nos. 1-7, the

relationship between the amount of antimony diacyl dithiocarbamate added and the metal fatigue life was observed, indicating that 0.1wt% or more has to be added to obtain the effect of prolongation of the fatigue life. Though the effect of addition of the carbamic acid salts increases with increase of the added amount, since the upper limit of the amount depends on solubility and raw cost of the carbamic acid salts used, it is preferred to use them at 5wt% or less. In Sample nos.7-20, the relationship between the amount of dithiocarbamic acid salts and the metal fatigue life was examined. In these tests, the added amount of the dithiocarbamic acid salts was made 1.0wt%, the metal and the hydrocarbon group in the salts were diversified, and a solubilizing agent was added in some cases. In any cases, it was found that the metal fatigue life was markedly prolonged in comparison with that of the oil for comparison. Particularly, the use of the solubilizing agent is highly effective in prolongation of the metal fatigue life as seen from Sample nos. 17, 19 and 20.

Table 1

Formulation (wt%)	Sample no. / Water-glycol flame retarded hydraulic oil	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
	Daphne Fire Proof 200G	99.95	99.90	99.85	99.80	99.70	99.50	99.0	98.0	98.0	99.0	99.0	98.0	99.0	99.0	99.0	99.0	98.0	99.0	98.0	97.0	100
	Antimony diamyl dithiocarbamate	0.05	0.10	0.15	0.20	0.30	0.50	1.0													1.0	
	Sodium dimethyl dithiocarbamate								1.0													
	Potassium dimethyl dithiocarbamate									1.0												
	Zinc dimethyl dithiocarbamate										1.0											
	Zinc dimethyl dithiocarbamate											1.0										
	Zinc dipropyl dithiocarbamate												1.0							1.0		
	Zinc dipropyl dithiocarbamate													1.0								
	Zinc diamyl dithiocarbamate														1.0							
	Zinc dihexyl dithiocarbamate															1.0						
	Zinc N-ethyl-N-phenyl dithiocarbamate																1.0					
	Zinc dibenzyl dithiocarbamate																	1.0				
	Zinc bis(hydroxyethyl)dithiocarbamate																		1.0			
	Polyoxyethylene laurylamine																			1.0	1.0	
	Diethylene glycol monobutyl ether																	1.0				
	1-Amino-2-propanol																				1.0	
	Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
	Metal fatigue life (minute)	97	329	372	413	451	466	508	495	327	399	400	410	430	490	500	471	559	444	532	670	74